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RPPR Final Report
as of 14-Feb-2019

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STEM Degrees: **STEM Participants:**

Major Goals: The major goal of this project was to purchase and install a tunable infrared, vibrational sum frequency generation (vSFG) spectrometer to benefit the research and teaching missions of the University of Iowa and neighboring institutions. There are several other groups in the U.S. that use vSFG to investigate interfacial phenomena, such as spontaneous organization of lipid bilayers, surfactancy, or mechanisms of heterogeneous catalysis. However, there was not a vSFG spectrometer available in the state of Iowa. This proposal aimed to provide researchers in this region access to vSFG, enabling higher quality research. The spectrometer is composed of a visible beam at 532 nm and tunable infrared laser. The spectrometer includes optics to direct these two beams to our sample substrates, where the photons are up-converted to the sum-frequency (sum = ir + vis). Sum-frequency photons are analyzed for polarization, selected for wavelength, and quantified by a photomultiplier tube. By scanning the wavelength of incident IR photons and monitoring intensity of the energy-matched SFG photons, an effective vibrational spectrum of exclusively interfacial species may be acquired. This spectrometer is turn-key including all optics, electronics, software, detection monochromator, and laser table.

Accomplishments: All major goals are accomplished. The vSFG spectrometer is purchased and installed in our laboratory. Preliminary data using the SHG and vSFG modes of the instrument are attached to this report via the uploaded file for two projects. These data serve two research projects in my group. One is the interrogation of solid / ionic liquid interfaces. This project includes thin (ca. 1 ?m) films of ILs on metallic substrates, allowing unprecedented spectroscopic measurements of the interface and surface-induced phase transitions. Our preliminary data includes SFG data that provides dynamic measurements of these phase transitions, which result in non-centrosymmetric environments that are SFG active. The transitions can take tens of minutes to achieve, and the SFG is an ideal tool to track the transition in a non-invasive way. Our work with ionic liquids also includes spectroelectrochemical studies of ionic liquid structures within their stable electrochemical windows. We are in the process of studying the hysteresis of capacitive response in IL media, and the vSFG provides crucial, molecular level details on molecular (re)orientation under an applied electrochemical bias. The final project that is benefiting from this work is the physical and chemical characterization of naturally occuring, environmental surface films. These films range in thickness from single nanometers to several microns, and characterization of the thinnest films is significantly aided by vSFG. We are particularly interested in the hydrogen bonding character of water molecules in these films, and the vSFG is the ideal tool to investigate this aspect of the environmental film. In addition to our own work we are beginning two collaborations with other faculty. One is with Prof. Wenyu Huang at Iowa State University using this SFG instrument to study electrocatalysts for methanol oxidation. The other is with Prof Claudio Margulis, Prof. Fatima Toor, and Prof Chris Cheatum at the University of Iowa to examine the effects of nano-scale confinement on ionic liquid materials.

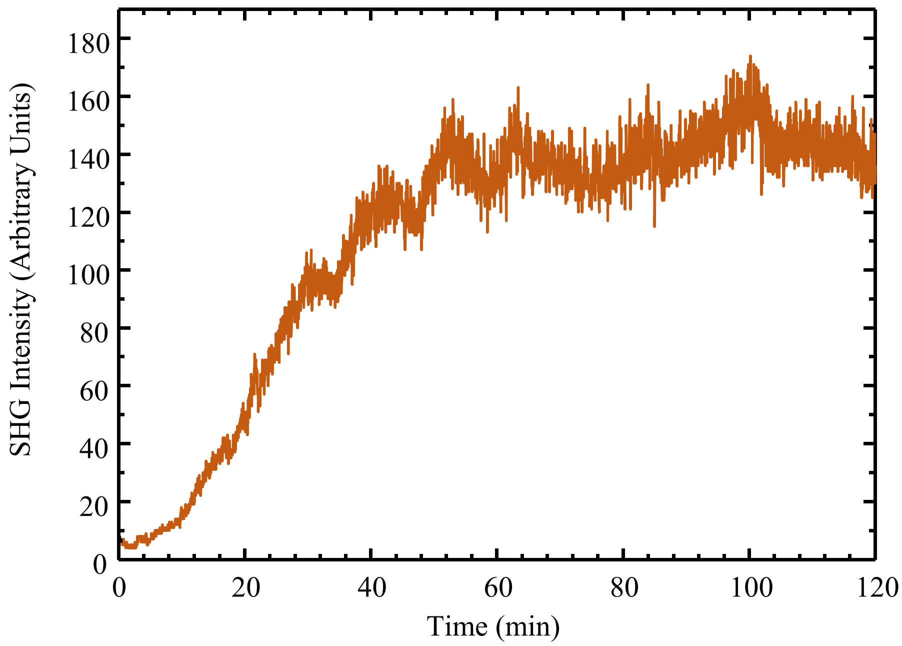
Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

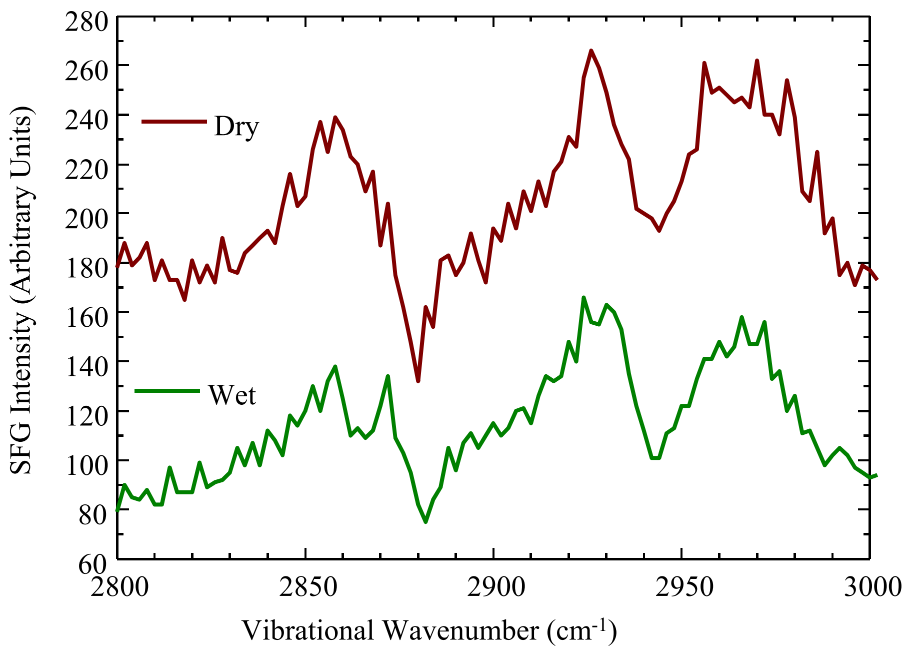
Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

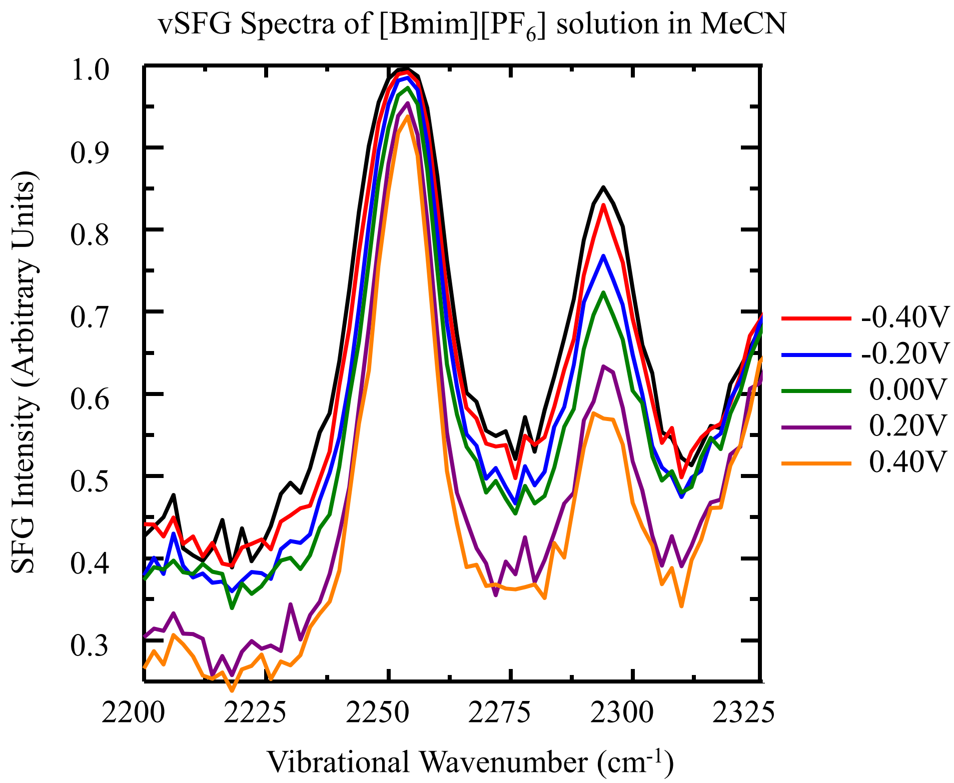


A plot of time vs. second harmonic generation intensity for an ionic liquid (BMIM OTF) film maturing on an Ag surface. The increased SHG intensity with time indicates increasing portion of the IL film is in a non-centrosymmetric (ordered) state. The maturation time, ca. 50 minutes, is similar to that observed in the absorption features from reflection infrared analysis of the same chemical system.



vSFG spectra displaying characteristic spectral features for a model environmental film composed of $MgSO_4$, eicosane, and stearic acid at 50%, 25%, and 25 % by mass respectively.

The top (red) spectrum is for a freshly prepared film immediately after drying. The lower (green) spectrum shows the same film after 24 hours exposure to a humid environment. Slight changes in CH_2 symmetric stretching (2850 cm^{-1}) and the CH_3 symmetric stretching (2871 cm^{-1}) as well as the narrowing of CH_3 asymmetric in and out of plane modes (2955 and 2965 cm^{-1} respectively) indicate the film is stable during water uptake (not washed away) and may experience slight increases in ordering of aliphatic domains.



Preliminary vSFG data collected on a 1:1 mixture of [Bmim][PF_6] on a Polycrystalline Au working electrode. The peak at 2280 cm^{-1} corresponds to the C≡N stretch of the MeCN, and decreases in intensity as the electrode potential is stepped from negative to positive values. This suggests the MeCN is displaced from the surface at more positive potentials. Data were collected at 4 cm^{-1} resolution. Potentials are reported against a Ag/Ag^+ reference electrode.

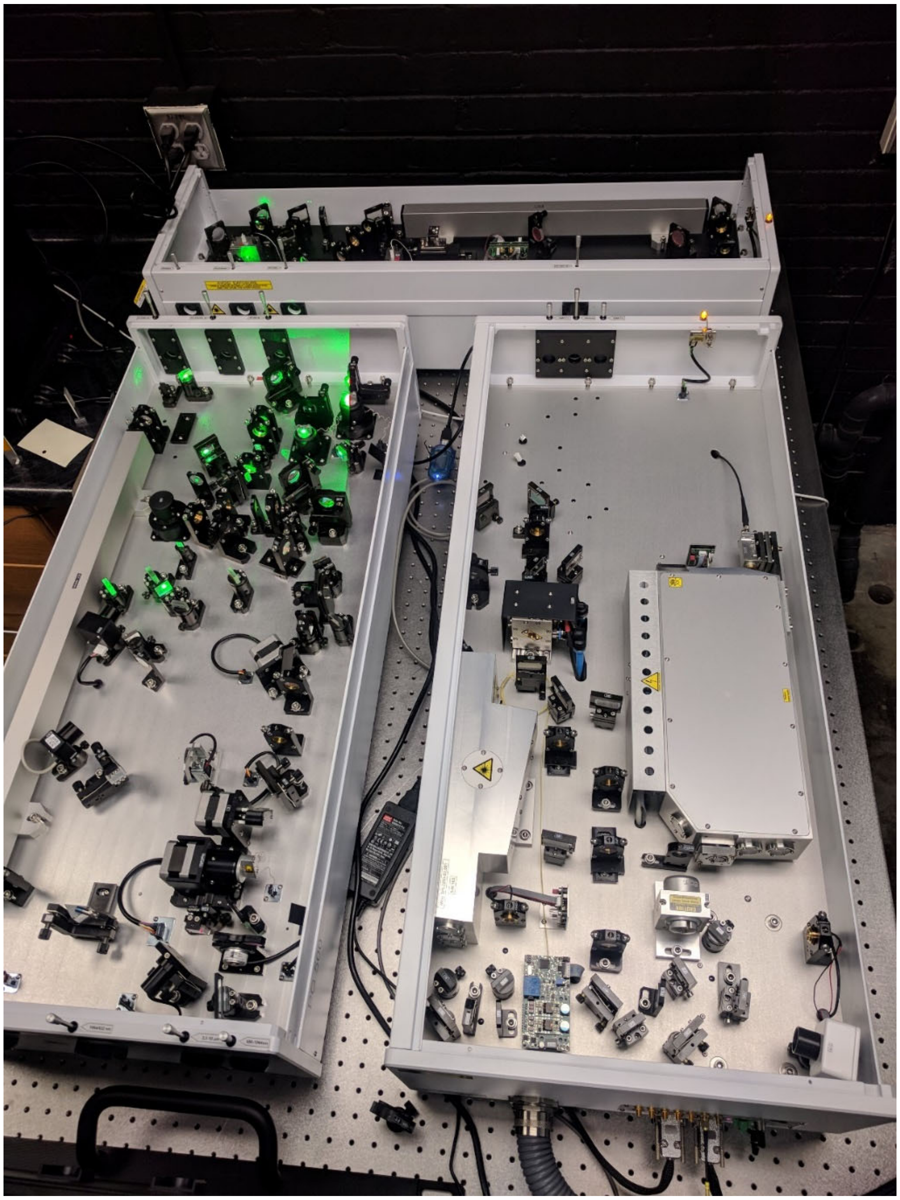


Image of the oscillator, amplifier, and difference frequency optics of the SFG spectrometer.

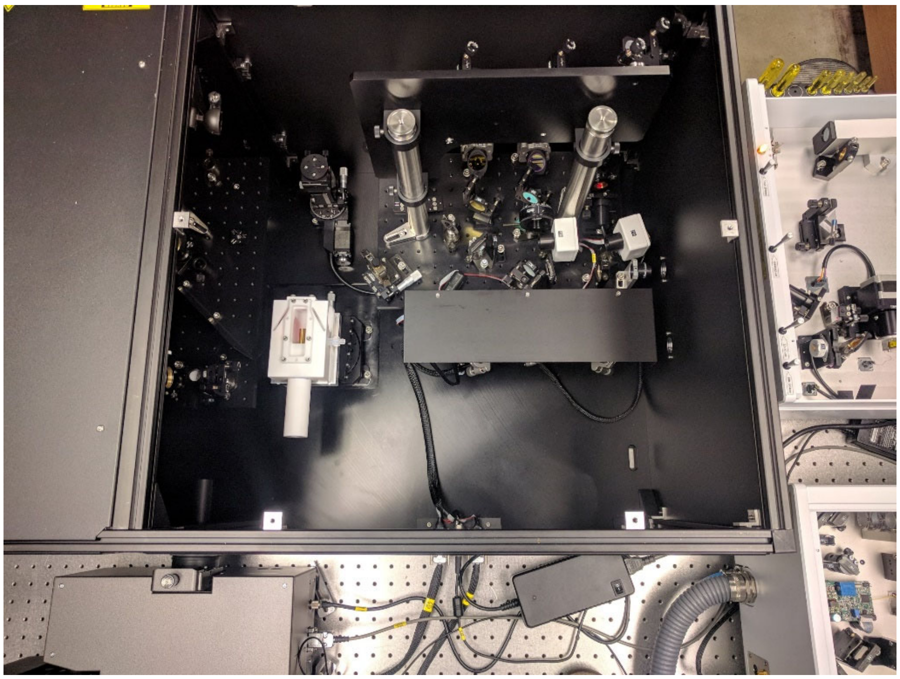


Image of the sampling chamber of the SFG spectrometer arranged for samples in the vertical plane. The white cell block at bottom left is our sampling chamber. We have installed optics to allow sampling in the horizontal plane as well.